different conditions. However, the prediction of ion exchange properties on the basis of the structure of the exchanger alone may become more readily possible through the use of computer modelling.

The study of ion exchange behaviour under the influence of microwave radiation is an area which preliminary research has suggested may be interesting.

*See also:* **II/Ion Exchange:** Historical Development; Novel Layered Materials: Non-Phosphates; Organic Ion Exchangers; Theory of Ion Exchange.

## Further Reading

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# Multispecies Ion Exchange Equilibria

*See* **II / ION EXCHANGE / Surface Complexation Theory: Multispecies Ion Exchange Equilibria**

# Non-Phosphates: Novel Layered Materials

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*See* **II / ION EXCHANGE / Novel Layered Materials: Non-Phosphates**

# Novel Layered Materials: Phosphates

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It has long been known that many polyvalent cations can be precipitated as amorphous phosphates from dilute solutions and these salts are useful in gravimetric analysis. More recently it has been recognized that many of these precipitates contain exchangeable acid protons and behave as inorganic ion exchangers. Phosphates of tetravalent metals such as Zr(IV), Ti(IV) and Sn(IV) have been found to possess high ion-exchange capacity and good stability in acid and oxidizing solutions and when exposed to high temperatures and ionizing radiation. Because of these properties, their potential uses for the purification of nuclear reactor cooling water or for the treatment of radioactive waste were investigated during the late 1950s and early 1960s, especially in nuclear centres. The ion-exchange properties of amorphous zirconium, titanium and tin phosphates were reviewed by Amphlett in 1964. However, the beginning of the chemistry of layered phosphates may be dated back to 1964, when Clearfield and Stynes refluxed zirconium phosphate gel in phosphoric acid solutions in an attempt to produce a material which was more resistant to hydrolytic attack than the original gel. The microcrystals obtained were found to possess a layered structure, called the $\alpha$-type, and with the composition $Zr(HPO_4)_2 \cdot H_2O$. This compound was indeed more resistant to hydrolytic attack than the amorphous analogue. It possesses two exchangeable protons per formula weight and is an excellent intercalating agent of protophilic species and a pure solid-state protonic conductor. Moreover, it is possible to correlate the observed properties with the structural

features. These findings stimulated research on the synthesis of layered phosphates of other polyvalent metals. The progress made up to 1982 was reviewed by Clearfield, and by Alberti and Costantino, and from that date the field of layered phosphates has been continuously expanding with the discovery and resolution of the structure of new crystalline phases. It was found that zirconium (or titanium) phosphate has an isomorphous modification, named $\gamma$-type, and the composition $Zr(PO_4)\ (H_2PO_4)\cdot 2H_2O$. This compound, as well as having cation exchange and intercalation properties, undergoes a topotactic anion exchange reaction of the dihydrogenphosphate groups with other anions. Most recently, the preparation of a new crystalline layered phase, named $\lambda$-type, and having the composition $Zr(PO_4)Cl(CH_3)_2SO$, has opened new research possibilities. This article deals with the preparation, structure, ion exchange and intercalation properties of layered phosphates and phosphonates of polyvalent metals, mainly zirconium, and with their application. Exfoliation of layered phosphates which allows the preparation of mixed layered phosphates or thin-layer coatings on substrates such as silica and alumina or of microporous pillared layered phosphates will be described.

However, before discussing in more detail the above-mentioned materials, it is worth commenting briefly on the preparation, ion exchange properties and application of amorphous zirconium phosphate, because of its commercial availability and renewal of interest in its use in nuclear waste treatment.

Amorphous zirconium phosphate is easily prepared by adding a solution of zirconium salts to a solution of phosphoric acid in acid media (2–4 mol dm$^{-3}$ HCl). The precipitate can be appropriately treated to obtain the exchanger in glassy, granular or powdered form. The composition is best described by the formula $Zr(HPO_4)_{2-x}(OH)_{2x}\ nH_2O$, $x$ ranging between 0 and 0.2. The material is stable up to 180°C (temperature at which condensation of phosphates to pyrophosphates starts) in acidic medium (e.g. 6 mol dm$^{-3}$ $HNO_3$), and has a remarkable resistance to strong doses of ionizing radiation. The ion exchange capacity ranges from 4 to 6 mequiv. g$^{-1}$. At low loading, the exchanger prefers cations with lower hydrated ionic radius and higher charge. Its use for the selective removal of $^{137}Cs$ and $^{89}Sr$ radioisotopes from aqueous nuclear wastes in ultrafiltration and fluidized bed systems has been proposed. Amorphous zirconium phosphate, because of its bio-compatibility and high insolubility, is used to fill cartridges for the removal of urea from blood in haemodialysis machines.

## Layered Phosphates of Groups 4 and 14, 5 and 15 elements

### Preparation

Numerous layered phosphates of the elements of the groups 4, 5, 14 and 15 of the periodic table have been synthesized and many of them are listed in **Table 1**, together with their interlayer distance, the free area

**Table 1** Formulae and some properties of layered phosphates of groups 4, 14 and 5, 15 elements

| *Formula* | *Density (g cm$^{-3}$)* | *Ion exchange capacity (mmol H$^+$ g$^{-1}$)* | *Interlayer distance (Å)* | *Free area (Å$^2$)** |
|---|---|---|---|---|
| $\alpha$-$Ti(HPO_4)_2\cdot H_2O$ | 2.61 | 7.76 | 7.56 | 21.6 |
| $\alpha$-$Zr(HPO_4)_2\cdot H_2O$ | 2.72 | 6.64 | 7.56 | 24.0 |
| $\alpha$-$Hf(HPO_4)_2\cdot H_2O$ | – | 5.15 | 7.60 | 23.7 |
| $\gamma$-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$ | 2.37 | 7.25 | 11.60 | 16.5 |
| $\gamma$-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ | 2.43 | 6.27 | 12.20 | 17.8 |
| $\alpha$-$Si(HPO_4)_2$ | – | 8.90 | 7.4 | – |
| $\alpha$-$Ge(HPO_4)_2\cdot H_2O$ | – | 7.07 | 7.75 | – |
| $\alpha$-$Sn(HPO_4)_2\cdot H_2O$ | 3.12 | 6.08 | 7.80 | 21.4 |
| $\alpha$-$Pb(HPO_4)_2\cdot H_2O$ | – | 4.79 | 7.95 | 21.5 |
| $ZrPO_4Cl(CH_3)_2SO$ | – | – | 10.2 | – |
| $VOPO_4\cdot 2H_2O$ | 2.4 | – | 7.41 | 38.5 |
| $VO(HPO_4)\ 0.5H_2O$ | 2.8 | 5.81 | 5.70 | 35.7 |
| $NbOPO_4\cdot 3H_2O$ | – | – | 8.04 | – |
| $HNb(PO_4)_2$ | – | 3.52 | – | – |
| $HTa(PO_4)_2\cdot 2H_2O$ | – | 2.45 | 9.48 | 46.0 |
| $HAs(PO_4)_2$ | 2.88 | 3.52 | 7.98 | 37.1 |
| $KSb(PO_4)_2$ | 3.50 | – | 8.47 | 19.6 |
| $HSb(PO_4)_2$ | – | – | – | – |
| $SbOPO_4$ | 4.42 | – | 6.34 | – |

*Area associated to each –OH group on the plane.

surrounding the surface phosphate groups, density and calculated ion exchange capacity. It may be seen that, except for carbon, α-type phosphates of all the elements of groups 4 and 14 have been obtained. They are prepared with procedures similar to those used to obtain $Zr(HPO_4)_2 \cdot H_2O$, that is, by refluxing the amorphous precipitates in phosphoric acid (10–12 mol $dm^{-3}$). An alternative procedure, especially used for Zr and Ti hydrogenphosphates, involves direct precipitation from solutions containing phosphoric acid and Zr (or Ti) fluoro-complexes. The degree of crystallinity of the precipitates may be controlled by modifying the velocity of removal of the complexing agent, as gaseous HF. With this method, crystals of millimetre dimensions have been obtained. Note that only Zr(IV) and Ti(IV) can form phosphate dihydrogenphosphates of γ-type. The preparation involves the slow decomposition of fluoro-complexes in an $NH_4H_2PO_4$ solution. The precipitate, e.g. $[Zr(PO_4)(NH_4HPO_4)]$, is then converted into its hydrogen form by treatment with HCl solution.

Tetravalent elements with large dimensions, such as Ce(IV) and Th(IV) do not give rise to layered phosphates of α- or γ-type. The acid phosphates of these elements have been obtained in fibrous form suitable for the preparation of fully inorganic, self-consistent papers, thin films or membranes. The acid phosphates of groups 5 and 15 elements have been obtained by dissolving the oxides in concentrated phosphoric acid and heating to 270°C. $HSb(PO_4)_2$ can be obtained by treating the potassium salt with a strong acid solution. Group 5 elements also produce non-acid layered phosphates of formula $XOPO_4$ (X = V, Nb, Ta) and structure similar to that of $Zr(PO_4)Cl(CH_3)_2SO$. Vanadyl phosphate is one of the rare examples of a layered phosphate which has a low electronic conductivity and is capable of redox intercalation reactions similar to those shown by graphite or layered dichalcogenides. Generally speaking, layered phosphates possess good chemical and thermal stability. Layered $Zr(HPO_4)_2 \cdot H_2O$ is a very insoluble compound, stable even in highly concentrated non-complexing acid solutions. The interlayer water is lost after prolonged heating at 110°C while the condensation water of monohydrogenphosphates to pyrophosphates is lost at 450–500°C. Molybdenum and some divalent cations such as Fe, Cd and Mn also form layered phosphates but their physical and chemical properties have not been investigated thoroughly.

## Structural Aspects

Layered solids are molecular crystals formed by the packing of giant planar macromolecules called layers or lamellae. The bonds between the atoms present in the layer are strong, primarily covalent, while those between the atoms of adjacent lamellae are weak, essentially of the van der Waals type. Thus, layered solids generally exhibit a high anisotropy in their physical properties. The reactivity of layered solids is shown by the intercalation reaction, that is, the reversible insertion of guest species into the interlayer region without appreciable modification of the structure of the lamellae which move apart to accommodate the guest species. Hence, the structural aspects of a layered solid are closely connected with the bidimensional structure of the layers. The Greek letter prefix that often indicates a layered phosphate is related to the layer structure. The structures of the layered phosphates listed in Table 1 will be illustrated with reference to the α-, γ- and λ-zirconium phosphates, but the phosphates of other elements have similar structures. Geometrical considerations indicate that bidimensional structures can be easily formed by concatenation through the vertices of $MO_6$ octahedra (M being the polyvalent metal) of suitable dimension, and of $PO_4$ tetrahedra. In the present case different concatenation gives rise to different layer structures.

Crystals of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ are monoclinic with $a = 9.060(2)$ Å, $b = 5.297(1)$ Å, $c = 15.14(3)$ Å, and $\beta = 101.71(2)$ Å, space group $P2_1/n$. The sequence of two layers is shown in **Figure 1**. Each layer may be described as the concatenation of $ZrO_6$ octahedra and $O_3POH$ tetrahedra. Note that each tetrahedron bridges three different octahedra and these, in turn, bridge six tetrahedra. The layer is a planar macromolecule bearing acid P–OH groups on the

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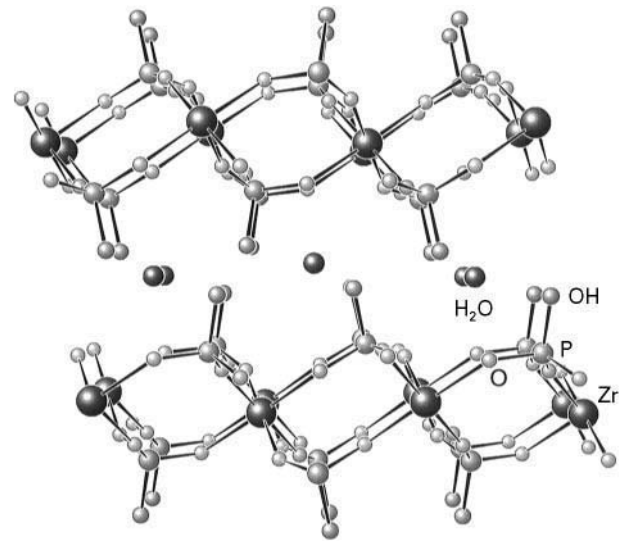


**Figure 1** Computer-generated representation of the sequence of two layers of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$. (Crystal data from Clearfield A and Smith GD (1969) *Inorganic Chemistry* 8: 431–436.)

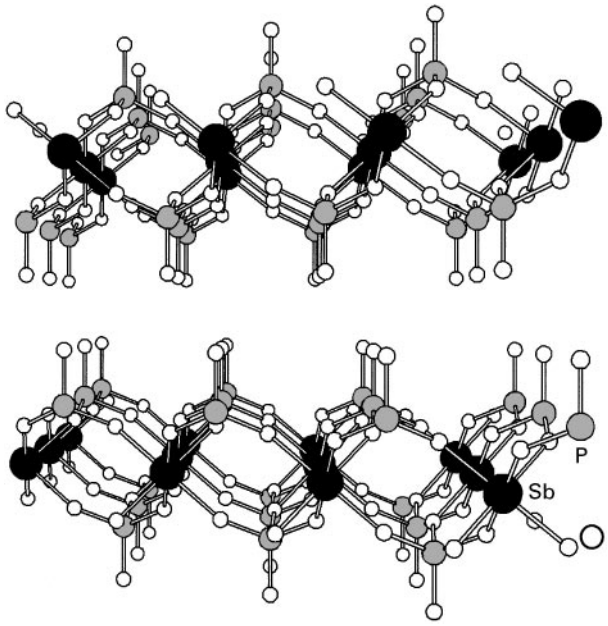


**Figure 2** Computer-generated representation of the sequence of two layers of $HSb(PO_4)_2$. (Crystal data from Piffard Y, Oyetola S, Courant S and Lachgar S (1985) *Journal of Solid State Chemistry* 60: 209–213.)

surfaces. The distance between adjacent phosphate groups on one side of the layer is 5.3 Å and the 'free area' around each P–OH group is 24 $Å^2$. The interlayer distance is 7.56 Å and the arrangement of the pendant phosphate groups creates six-sided cavities, each containing one water molecule, in the interlayer region. This layered structure is common to the other $\alpha$-layered phosphates and it is very similar to that of $HSb(PO_4)_2$, shown in **Figure 2**.

The second layer structure, in which two different tetrahedral species are used at the same time, is present in the $\gamma$-compound with formula $Zr(IV)(PO_4)(H_2PO_4)\cdot 2H_2O$. The $\gamma$-layer consists of two ideal planes containing zirconium atoms bonded by tetrahedral $PO_4$ and $H_2PO_4$ groups (see **Figure 3**). The $PO_4$ group shares all four oxygens with zirconium atoms while the $H_2PO_4$ shares two oxygens with two different Zr atoms and points the remaining two OH groups towards the interlayer region. The interlayer distance is 12.2 Å, and the free area surrounding the $P(OH)_2$ groups on the surface of the layers is 35 $Å^2$.

A third layer structure of great interest can be formed by bridging four different zirconium atoms with a tetrahedral $PO_4$ group in a slightly different manner from $\gamma$-zirconium phosphate, and then by balancing the residual positive charge and completing the octahedral configuration of each zirconium atom with a monovalent anionic ligand, $Cl^-$ and a neutral monodentate ligand, $(CH_3)_2SO$, as

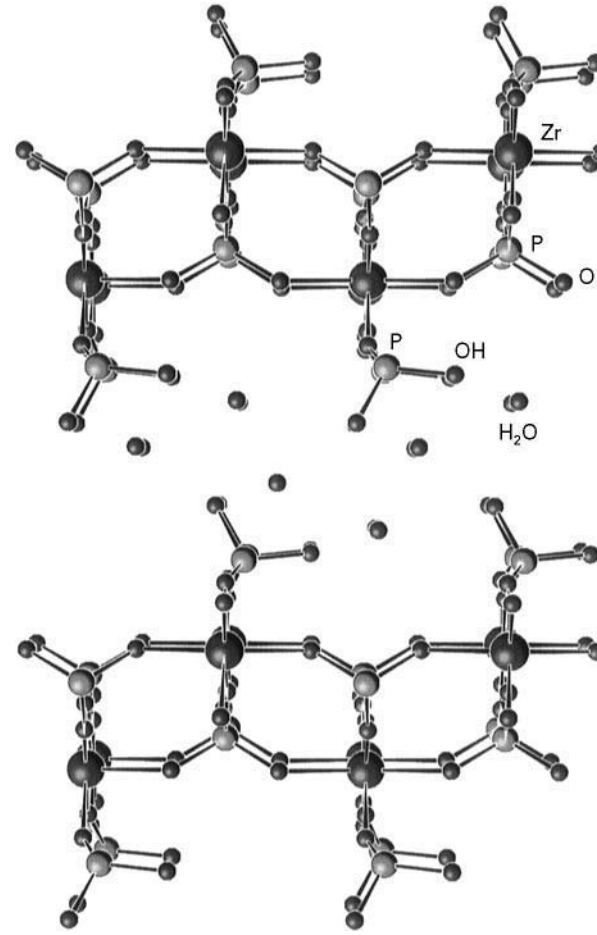


**Figure 3** Computer-generated representation of the sequence of two layers of $\gamma$-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$. (Crystal data from Christensen A, Andersen EK, Andersen IGK, Alberti G, Nielsen N and Lehman MS (1990) *Acta Chemica Scandinavica* 44: 865–872.)

illustrated in **Figure 4**. Note that this structure is essentially the same as that of layered vanadyl phosphate (see **Figure 5**) and of uranyl phosphate.

## Chemical Reactivity

### Ion Exchange Properties

The protons of layered acid phosphates are able to diffuse in the interlayer region and these compounds behave as inorganic cation exchangers and proton conductors. Mainly the ion-exchange properties of $\alpha$-$Zr(HPO_4)_2\cdot H_2O$ will be considered as these have been investigated extensively. However, the findings apply to the other members of the class. All these compounds are solid acids and the simplest way to completely replace the protons with other cations is by titrating the microcrystals with solutions of the hydroxide of the cation to be exchanged. The

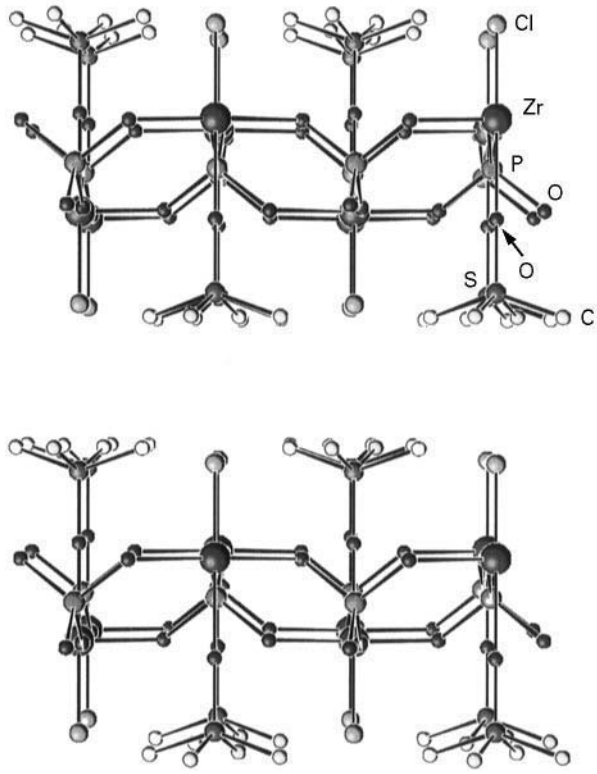


**Figure 4** Computer-generated sequence of two layers of $Zr(PO_4)Cl(CH_3)SO$. (Data from Alberti G, Bartocci M, Santarelli M and Vivani R (1997) *Inorganic Chemistry* 36: 3574–3575.)

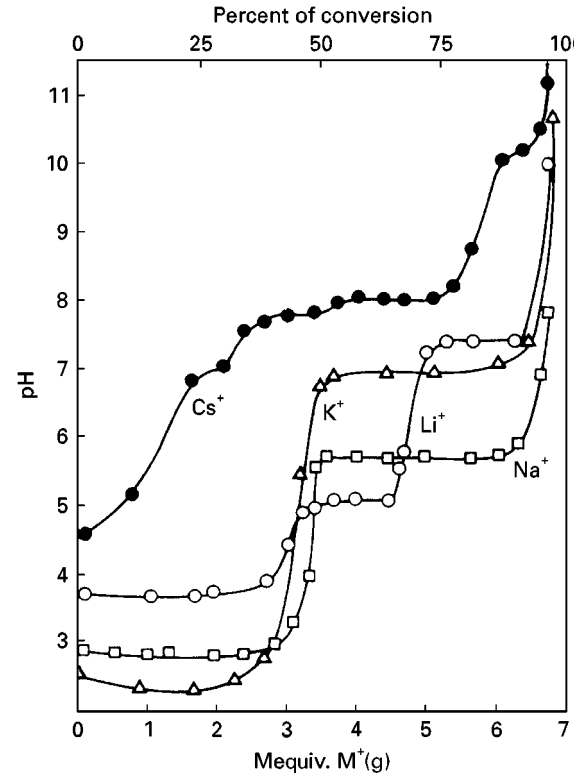


**Figure 6** Potentiometric titration curves of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ with the hydroxides of the indicated alkali metal ions, in the presence of the corresponding metal chlorides. (Reproduced with permission from Alberti G and Costantino U (1974) *Journal of Chromatography* 102: 5–29. Copyright: Elsevier Science Publishing, Amsterdam.)

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titration curves of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ with alkaline metal hydroxides, in the presence of the corresponding metal chloride, are shown in **Figure 6**.

It may be seen that the exchange process occurs stepwise. In each plateau of the titration curve the composition of the solution, and hence also the pH, is constant. Since temperature and pressure are also constant, the phase rule requires the presence of two solid phases. The X-ray diffraction patterns of samples with increasing metal ion loading indeed indicate the presence of two solid phases, one transforming into the other as the exchange reaction proceeds. According to a model developed by Alberti, ion exchange in the $\alpha$-phases takes place by diffusion of the cations from the external part of the layered crystals towards the bulk with an advancing phase boundary with the co-existence in the same crystallite of two phases. To illustrate the model consider $H^+/Na^+$ exchange (see Figure 6 and the scheme in **Figure 7**). Initially we observe the formation of a phase of composition $ZrHNa(PO_4)_2 \cdot 5H_2O$ and interlayer distance 11.8 Å, according to the reaction (the number in parentheses refers to the interlayer distance):

$$Zr(HPO_4)_2 \cdot H_2O\ (7.6\ \text{Å}) + Na^+ + 4H_2O \rightarrow$$
$$ZrHNa(PO_4)_2 \cdot 5H_2O\ (11.8\ \text{Å}) + H^+$$

The composition of the exchanged phase does not change until half the protons of the original hydrogen

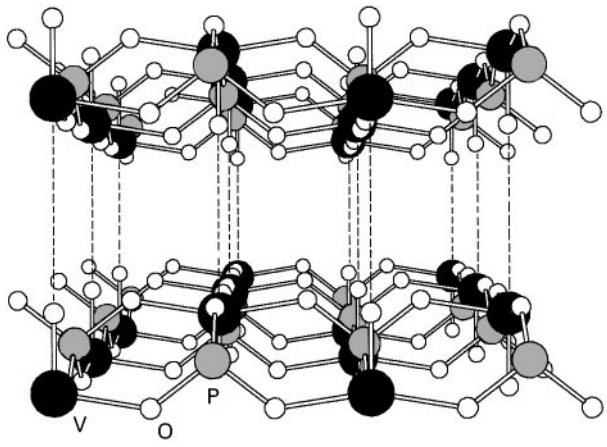


**Figure 5** Computer-generated structure of the sequence of two layers of $VOPO_4$. (Crystal data from Tietze HR (1981) *Australian Journal of Chemistry* 34: 2035–2038.)

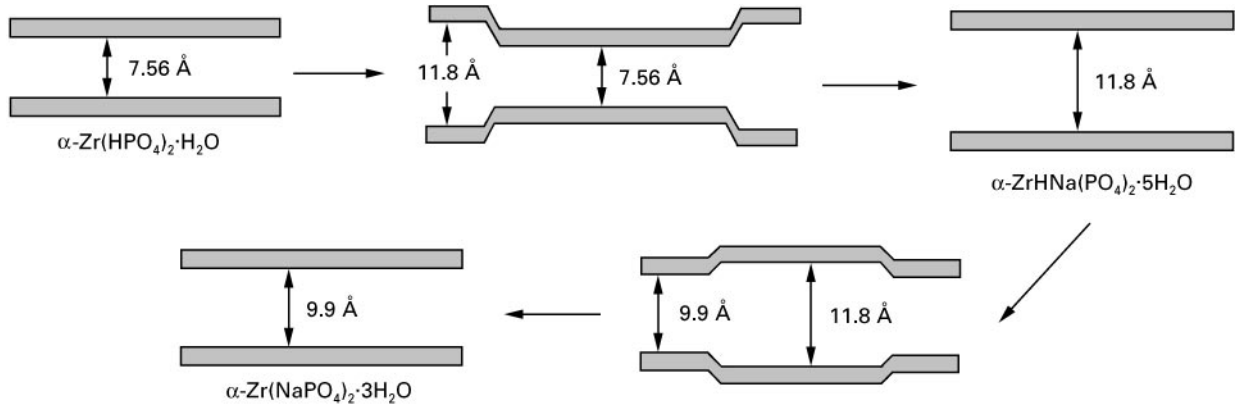


**Figure 7** Schematic representation of the phases formed during the $H^+/Na^+$ ion-exchange process in $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ microcrystals.

form have been replaced by $Na^+$ ions. At the end of the process only the monosodium form is present and the pH of the solution rises to a value at which the following reaction takes place:

$$ZrHNa(PO_4)_2 \cdot 5H_2O(11.8\ \text{Å}) + Na^+ \rightarrow$$
$$Zr(NaPO_4)_2 \cdot 3H_2O(9.9\ \text{Å}) + 2H_2O + H^+$$

Examination of the ion-exchange process

$$Zr(HPO_4)_2 \cdot H_2O + M^+ + (n-1)H_2O \rightarrow$$
$$ZrHM(PO_4)_2 nH_2O + H^+$$

where M is an alkaline metal, shows the following selectivity sequence: $K^+ > Na^+ > Li^+ \gg Rb^+ \cong Cs^+$, since potassium uptake occurs at pH $\cong$ 2 while $H^+/Cs^+$ exchange occurs at pH $\cong$ 7. The different selectivity towards $K^+$ and $Cs^+$ is a direct consequence of the structural features of the host. The zeolitic cavities present in the interlayer region of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$, are interconnected by windows of 2.64 Å width. Therefore, cations such as $Rb^+$ and $Cs^+$ that have an ionic diameter greater than 2.64 Å, as well as highly hydrated divalent and trivalent cations, are not taken up unless energy is supplied to spread the layers apart. Accordingly, a facile exchange of large monovalent ions or of highly hydrated divalent or trivalent cations takes place if precursors with a high interlayer distance such as polyhydrate zirconium phosphate, $Zr(HPO_4)_2 \cdot 4H_2O$ ($d = 10.4$ Å) or the monosodium form ZrHNa $(PO_4)_2 \cdot 5H_2O$ ($d = 11.8$ Å) or some intercalation compounds with alkanols or amines (see below) are employed. A study of the ion exchange isotherms of $ZrHNa(PO_4)_2 \cdot 5H_2O$ with different monovalent and divalent cations (see **Figure 8**) revealed the following selectivity order $Ba^{2+} > Ca^{2+} > Cs^+ > K^+ > Mg^{2+} > Na^+ > Li^+$.

By using suitable precursors, a large number of cations of the periodic table, as well as organic cations or cationic complexes, have been intercalated via ion exchange processes into zirconium phosphate and other layered phosphates. **Table 2** states the composition and interlayer distance of a selected number of phases, some of them prepared for practical applications. These layered phosphates possess good thermal resistance and are stable even when exposed to high doses of ionizing radiation.

Zirconium phosphate has been used to perform ion exchange processes in molten salts at high temperatures. **Figure 9** shows the $Na^+/K^+$ forward and reverse isotherms obtained in molten $NaNO_3$–$KNO_3$ mixtures at 450°C.

Good resistance to radiation makes these phosphates particularly suitable for the uptake of dangerous radionuclides such as $^{137}Cs^+$, $^{89}Sr^{2+}$ and $^{60}Co^{2+}$.

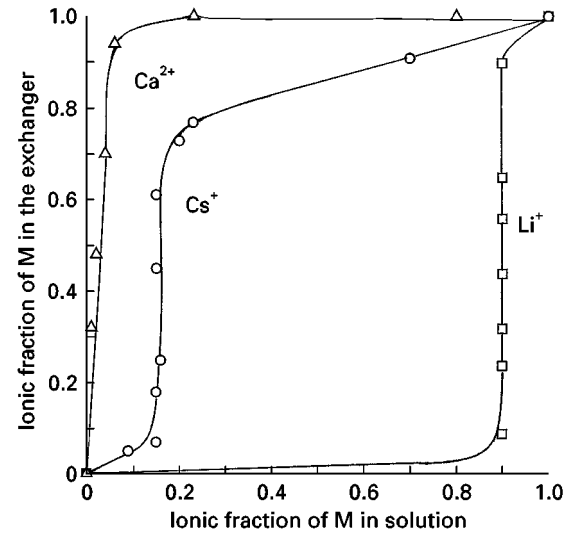


**Figure 8** Forward $Na^+/Ca^{2+}$, $Na^+/Cs^+$ and $Na^+/Li^+$ ion-exchange isotherms on $\alpha$-$ZrNaH(PO_4)_2 \cdot 5H_2O$. Concentration: 0.1 equiv $dm^{-3}$, temperature 25°C.

**Table 2** Formulae and interlayer distances of some anhydrous and hydrated salt forms of α-zirconium phosphate. Some exchanged forms with cationic complexes are also listed

| *Compound* | *Interlayer distance (Å)* | *Compound* | *Interlayer distance (Å)* |
|---|---|---|---|
| $ZrHLi(PO_4)_2 \cdot 4H_2O$ | 10.1 | $Zr(UO_2)_{0.9}H_{0.2}(PO_4)_2 \cdot 5H_2O$ | 10.5 |
| $Zr(LiPO_4)_2 \cdot 4H_2O$ | 10.0 | $ZrH_{0.4}Mg_{0.8}(PO_4)_2 \cdot 4H_2O$ | 9.8 |
| $Zr(LiPO_4)_2$ | 7.05 | $ZrH_{0.4}Mg_{0.8}(PO_4)_2$ | 7.9 |
| $ZrHNa(PO_4)_2 \cdot 5H_2O$ | 11.8 | $ZrBa(PO_4)_2 \cdot 2.5H_2O$ | 9.5 |
| $Zr(NaPO_4)_2 \cdot 3H_2O$ | 9.8 | $ZrMn(PO_4)_2 \cdot 4H_2O$ | 9.7 |
| $Zr(NaPO_4)_2$ | 8.42 | $ZrCo(PO_4)_2 \cdot 4H_2O$ | 9.6 |
| $ZrHK(PO_4)_2 \cdot H_2O$ | 8.02 | $ZrNi(PO_4)_2 \cdot 4H_2O$ | 9.55 |
| $Zr(KPO_4)_2 \cdot 3H_2O$ | 10.7 | $ZrCu(PO_4)_2 \cdot 4H_2O$ | 9.6 |
| $Zr(KPO_4)_2$ | 9.0 | $ZrZn(PO_4)_2 \cdot 4H_2O$ | 9.6 |
| $ZrHCs(PO_4)_2 \cdot 2H_2O$ | 11.3 | $Zr[Cr(NH_3)_6]_{0.25}H_{1.25}(PO_4)_2$ | 10.8 |
| $Zr(CsPO_4)_2 \cdot 6H_2O$ | 14.2 | $Zr[Co(C_5H_5)_2]_{0.5}H_{1.5}(PO_4)_2$ | 12.0 |
| $Zr(CsPO_4)_2$ | 9.5 | $Zr[Pt(NH_3)_4]_{0.5}H(PO_4)_2$ | 10.6 |
| $Zr(AgPO_4)_2$ | 8.4 | $Zr[Cu(bpy)]_{0.5}H(PO_4)_2$ | 14.5 |
| $ZrZn(PO_4)_2$ | 7.66 | $Zr[Cu(phen)]_{0.5}H(PO_4)_2$ | 15.8 |
| $ZrH_{0.5}Cr_{0.5}(PO_4)_2 \cdot 4H_2O$ | 11.6 | $Zr[Pd(dmp)]_{0.5}H(PO_4)_2$ | 17.3 |
| $ZrRh_{0.66}(PO_4)_2 \cdot 4H_2O$ | 11.6 | $Zr[Fe(C_5H_5)_2]_{0.2}H_{1.8}(PO_4)_2$ | 11.6 |
| $Zr(VO)_{0.5}H(PO_4)_2 \cdot 3H_2O$ | 9.75 | $Zr[Cu(NH_3)_4]_{0.6}H_{0.8}(PO_4)_2$ | 9.6 |

bpy = bipyridyl; phen = phenantroline; dmp = dimethylphenantroline.

In addition, zirconium phosphates exchanged with transition metal ions are heterogeneous catalysts and supports for chromatographic separation. For the latter application it should be noted that layered acid phosphates are usually obtained as small platelets ($\sim 1\ \mu m$) and very compact chromatographic columns are usually obtained. The flows are therefore slow while some particles tend to be released into the external solution. This problem may be overcome by using larger particles, even though the rate of exchange decreases, or by supporting the layers on a suitable support such as silica gel.

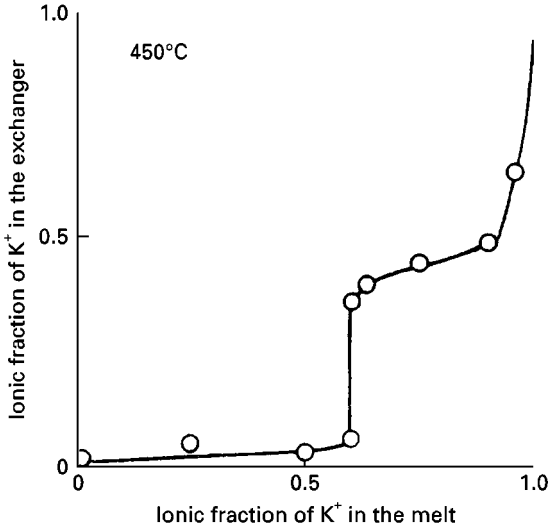


**Figure 9** Forward and reverse $Na^+/K^+$ ion-exchange isotherms on layered α-zirconium phosphate in molten $NaNO_3$–$KNO_3$ mixtures at 450°C. (Reproduced with permission from Alberti G and Costantino U (1974) *Journal of Chromatography* 102: 5–29. Copyright: Elsevier Publishing Science, Amsterdam.)

**Topotactic anion exchange reactions** We have seen above that the majority of layered phosphates are inorganic cation exchangers. Layered phosphates of the γ-type show a typical reaction, which formally represents an anion exchange process. A topotactic exchange reaction is defined as the replacement of one group by another without alteration of the host matrix. If we consider the structure of the γ-phases we observe that the dihydrogenphosphate groups, present on the surface of the lamellae, have a net charge of $-1$, delocalized over two oxygen atoms. The $H_2PO_4^-$ is weakly bonded to the central tetravalent atom (Zr or Ti) and it may be easily replaced by other suitable groups, when the layered phosphate is equilibrated with a solution containing such groups. Topotactic exchange reactions with phosphites, hypophosphites, phosphonates or phosphinates, according to the general reaction:

$$Zr(PO_4)(H_2PO_4) \cdot 2H_2O + RPO_2OH^- \rightarrow$$
$$Zr(PO_4)(RHPO_3) \cdot nH_2O + H_2PO_4^- + (2-n)H_2O$$

are particularly efficient. R is an aliphatic or aromatic organic moiety that may bear a functional group. This simple procedure has allowed the preparation of a large number of new layered phosphate–phosphonates of γ-type with very interesting properties.

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### Intercalation Properties

Over time, research on layered phosphates has moved from the study of their ion exchange properties to that of their intercalation properties in great part determined by the presence of Brønsted acid groups in the interlayer region. Both α- and γ-zirconium phosphates are excellent intercalating agents of Lewis bases. The intercalation chemistry of the former has been more widely investigated and we will be mainly concerned with α-zirconium phosphate. Many molecules belonging to various classes of organic compounds (alkanols, glycols, alkyl and aryl amines, heterocyclic bases, aminoacids and dyes) have been intercalated. The corresponding intercalation compounds have been characterized for composition and arrangement of the guest molecules in the interlayer region. **Table 3** gives the interlayer distance and composition of some typical examples of intercalation compounds.

Let us examine in more detail the intercalation of n-alkylamines that leads to the formation of compounds containing two moles of guest per mole of host, according to the reaction

$$\alpha\text{-}Zr(HPO_4)_2 \cdot H_2O + 2RNH_2 \rightarrow$$
$$\alpha\text{-}Zr(HPO_4)_2 \cdot 2RNH_2 \cdot H_2O$$

where R is the n-alkyl-chain. The reaction proceeds stepwise with the formation of different phases. At low amine loading we observe the formation of a phase with interlayer distance 10.4 Å and the alkyl-chain axis is almost parallel to the layer plane (see **Figure 10A**). At half intercalation, the alkyl chains are arranged as a monolayer of extended molecules with the chain axes inclined by 55° with respect to the layer plane (see Figure 10B). At full intercalation n-alkylamines give rise to compounds in which the inorganic layer regularly alternates with a bilayer of alkylamines with the n-alkyl chain in *trans–trans* conformation (see Figure 10C). The terminal $-NH_2$ groups are protonated by the hydrogenphosphate groups.

Intercalation compounds with α,ω-alkyldiamines contain one mole of guest per formula weight. The guest molecules are arranged as a monolayer of extended chains and the terminal $-NH_2$ groups interact with the P–OH groups belonging to two-faced layers. Alkanols and glycols produce intercalation compounds whose composition and arrangement of guest species are similar to those found in alkyl monoamines and diamines, respectively. However, direct intercalation is prevented by the lower basicity of the alkanol OH group, compared to that of the $NH_2$ group. It is necessary to use as precursors pre-swelled zirconium phosphates.

**Table 3** Interlayer distances and guest contents of intercalation compounds of α-zirconium phosphate

| *Guest molecule* | *mol Guest/ mol α-ZrP* | *Interlayer distance (Å)* |
|---|---|---|
| Methylamine | 2.0 | 12.1 |
| Ethylamine | 2.0 | 14.8 |
| Propylamine | 2.0 | 17.6 |
| Penthylamine | 2.0 | 21.5 |
| Diethylamine | 1.0 | 12.7 |
| Dipropylamine | 1.0 | 15.7 |
| Dioctylamine | 0.8 | 26.8 |
| Aniline | 2.0 | 18.4 |
| *p*-Methoxyaniline | 2.0 | 21.7 |
| Benzylamine | 2.0 | 19.1 |
| Benzylethylamine | 2.0 | 22.4? |
| Ephedrine | 2.0 | 22.0 |
| Histamine | 1.9 | 20.5 |
| Pyridine | 0.95 | 10.9 |
| Pyrazole | 0.75 | 10.8 |
| Imidazole | 0.95 | 10.7 |
| 3-Methylpyrazole | 0.98 | 12.1 |
| 1-Methylimidazole | 0.58 | 10.4 |
| Benzimidazole | 1.90 | 20.4 |
| Pyridazine | 0.64 | 10.8 |
| Pyrimidine | 0.71 | 11.1 |
| Pyrazine | 0.78 | 10.8 |
| 2,2′-Bipyridyl | 0.25 | 10.9 |
| 1,10-Phenantroline | 0.5 | 13.6 |
| 2,9-Dimethylphenantroline | 0.5 | 14.6 |
| Ethanol | | 14.2 |
| 1-Propanol | | 16.6 |
| 1-Butanol | | 18.7 |
| 1-Octanol | | 26.7 |
| Isopropanol | | 15.6 |
| 2-Methyl-1-propanol | | 17.5 |
| 3-Methyl-1-butanol | | 19.2 |
| Benzyl alcohol | | 21.0 |
| Diethylene glycol | | 10.5 |
| Acetone | | 9.9 |
| Acetylacetone | | 13.5 |
| Acetonitrile | | 11.3 |
| Urea | 0.9 | 9.9 |
| α-Alanine (DL) | 0.5 | 12 |
| Phenylalanine (DL) | 1.7 | 23.2 |
| Histidine (DL) | 0.9 | 16.2 |
| Crystal violet | 0.5 | 22 |
| Rhodamine | 0.66 | 24.7 |

Heterocyclic bases give rise to non-stoichiometric intercalation compounds and the heterocyclic ring is positioned parallel to the layer plane. For the arrangement of other intercalated guests the reader is referred to recent reviews given in the Further Reading section. Materials with special properties have also been obtained by intercalation. Porphyrins and metalloporphyrins, thionine, methylene blue and rhodamine have been intercalated in α-zirconium phosphate and the materials obtained have been investigated for their optical properties. The possibility of intercalating dyes and of controlling, at least to

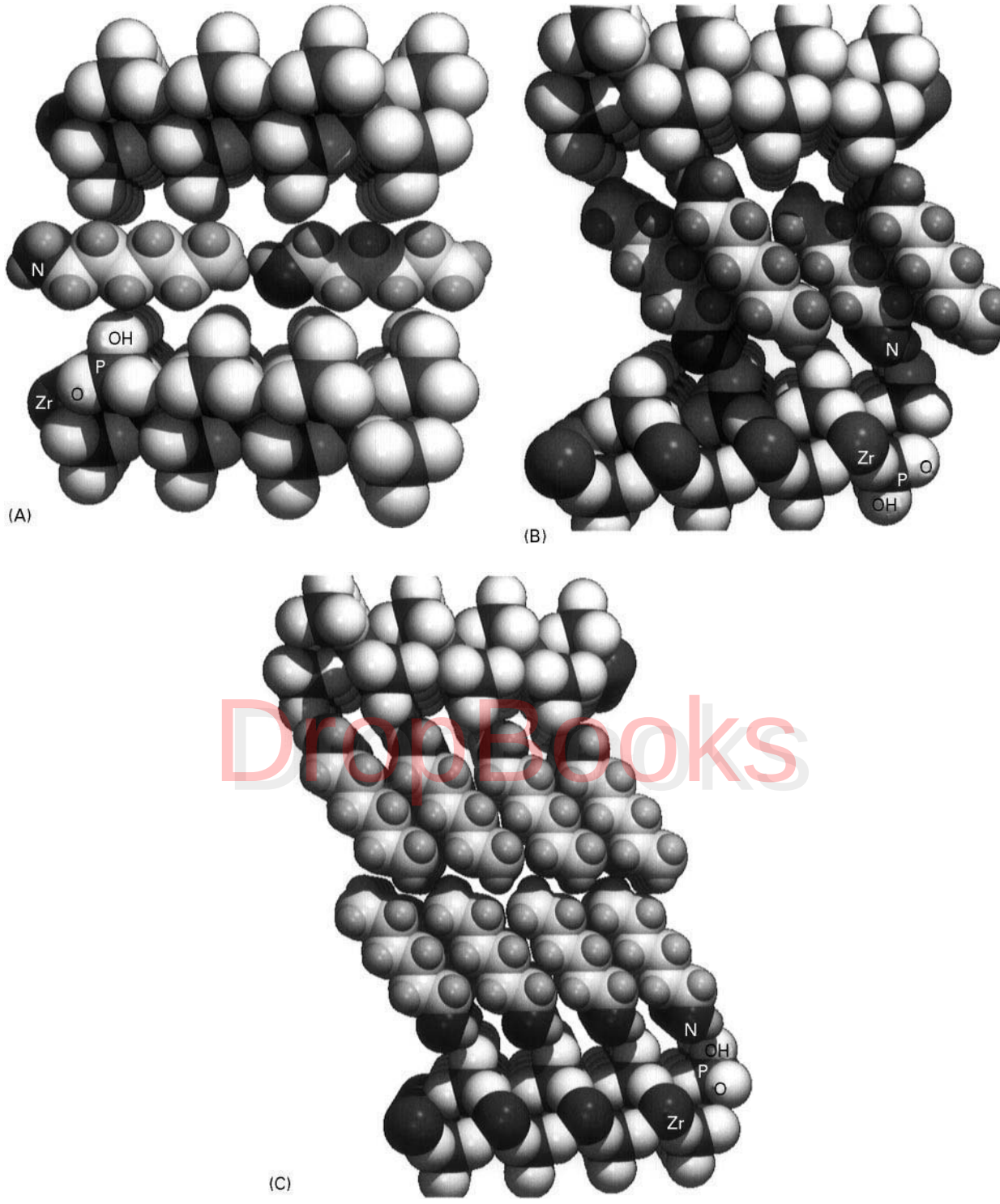


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**Figure 10** Arrangement of n-alkyl monoamines intercalated into $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$: (A) alkyl-chain axis parallel to the layer plane. (B) Monolayer of extended molecules in *trans–trans* conformation. (C) Bilayer of extended molecules in *trans–trans* conformation.

some extent, molecular orientation is of interest in the preparation of new composite materials for non-linear optic applications. Intercalation of weak Brønsted bases was found to enhance the proton conduction of the host and some of the compounds obtained have been used as active components in solid-state electrochemical gas sensors. Molecular and chiral recognition properties have been induced

in layered zirconium phosphate by the intercalation of suitable receptors such as aminated $\beta$-cyclodextrins, crown ethers or a Pirkle receptor.

Much attention is presently being paid to the possibility of performing reactions in the interlayer region. Polymerization, induced by chemical, thermal or photochemical treatment, of pyrrole, aniline, propargylamine or $\varepsilon$-aminocaproic acid intercalated in layered phosphates, produces interesting composite materials in which the inorganic layers regularly alternate with the polymers formed in the interlayer region.

## Exfoliation Process

We have seen that layered polyvalent metal phosphates are obtained as molecular crystals built up by the packing of the layers which are planar macromolecules. These bidimensional macromolecules are usually very thin (5–15 Å), whereas planar dimensions are of the order of $\mu m^2$, depending on the conditions of synthesis. If a layered crystal is exfoliated in single layers, materials with a very large surface area and with enhanced reactivity are obtained. For example, the complete exfoliation of 1 g of $\alpha$-zirconium phosphate will produce material with a surface area of 950 $m^2$. Furthermore, the suspension of the layers may be used to obtain thin films and pellicles or to cover suitable supports.

It is well known that layered smectite clays undergo so-called 'infinite swelling', that is, they disintegrate into single layers or packets of a few layers, when suspended in water. This phenomenon has never been observed in layered phosphates probably because of stronger layer–layer interactions. However, intercalation has made it possible to exfoliate both $\alpha$- and $\gamma$-zirconium phosphates. In the case of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ and of the other $\alpha$-type layered phosphates a good exfoliation has been obtained by the intercalation of short-chain alkylamines, such as methylamine or propylamine at 100% and 50% loading, respectively. This exfoliation process is shown schematically in **Figure 11**.

$\gamma$-$Zr(PO_4) \cdot (H_2PO_4) \cdot 2H_2O$ is best exfoliated when treated with dimethylamine. Colloidal dispersions containing highly anisotropic particles of nanoscale dimensions have a number of potential applications. After treatment with acids, flocculation allows the formation of completely inorganic pellicles or films useful in assembling the sensor layer of solid-state gas sensors, or to cover glass surfaces for chromatographic application. Composites of layered phosphates and silica gels or pillared layered phosphates have also been prepared from colloidal dispersions.

**Solid dispersions of layered phosphates in silica gel** Solid dispersions of $\alpha$- or $\gamma$-zirconium phosphates in porous silica can be prepared starting from mixtures of a tetrapropylammonium oligosilicate solution and zirconium phosphates, previously exfoliated with amines. They are formed after gelification of the mixture with acetic acid and subsequent calcination at 650°C to remove the organic moieties. At this temperature zirconium phosphates are transformed into layered pyrophosphates, but non-condensed phosphate groups are still present on the free surfaces of the lamellae. Accordingly, the composites obtained have a large surface area (350–500 $m^2\,g^{-1}$), good surface ion-exchange capacity and acid catalytic properties. Such composites may find application as stationary phases in chromatography.

**Pillared layered phosphates** The success obtained in the pillaring of clays to obtain microporous solids with larger pore diameters than those found in zeolites has stimulated research in preparing pillared layered structures based on metal(IV) phosphates. Synthetic strategy requires the insertion of large organic or inorganic cations (pillars) between the layers to prop them apart. If the pillars are sufficiently spaced, a microporous structure is obtained and the dimensions of the channels or diffusion paths are determined by the size of the pillars and their spacing in the interlayer region (see **Figure 12**).

Inorganic pillars are preferable to organic pillars because of their much higher thermal stability. To obtain thermally stable structures, pillaring has been performed with highly charged polyoxycations such as the $Al_{13}$ Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, or $[Zr(OH)_2(H_2O)_4]_4^{8+}$, or inorganic clusters such as $[Nb_6Cl_{12}]^{2+}$. After suitable thermal treatment, the layered phosphates contain as pillars, aggregates of inorganic oxides which have considerable thermal stability. The problem of inserting such large pillars has often been overcome by contacting the solution of the pillaring species with colloidal dispersions containing single layers, or packets of a few layers, of tetravalent metal(IV) phosphates. This provides access to the surface POH groups, the exchange reaction and the flocculation of the pillared material. However, the problem of achieving uniform pillar spacing to obtain a narrow distribution of micropores of predictable dimensions has not been completely resolved. The topic is of great interest since materials for molecular sieving and for shape-selective catalysis might result.

## Metal(IV) Phosphonates

A fundamental step in the development of the chemistry of layered phosphates was made in 1978

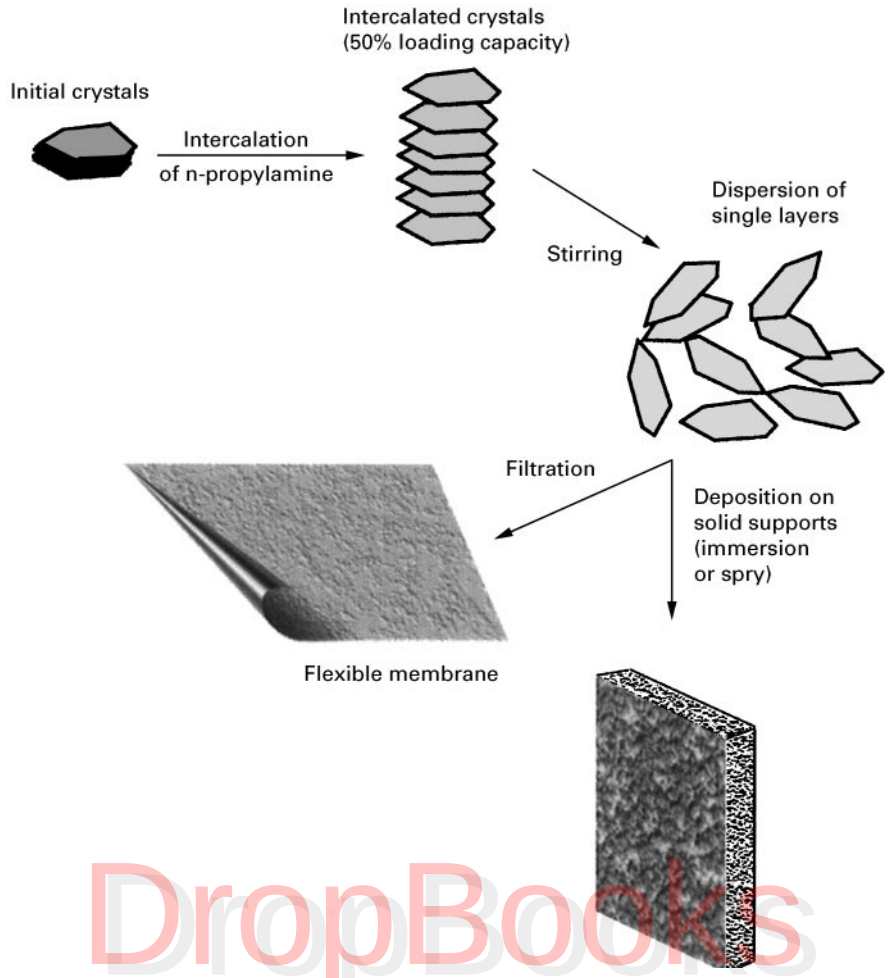


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**Figure 11** Schematic representation of the exfoliation of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ microcrystals by intercalation of n-propylamine. The formation of completely inorganic films or the coating of solid surfaces is also reported.

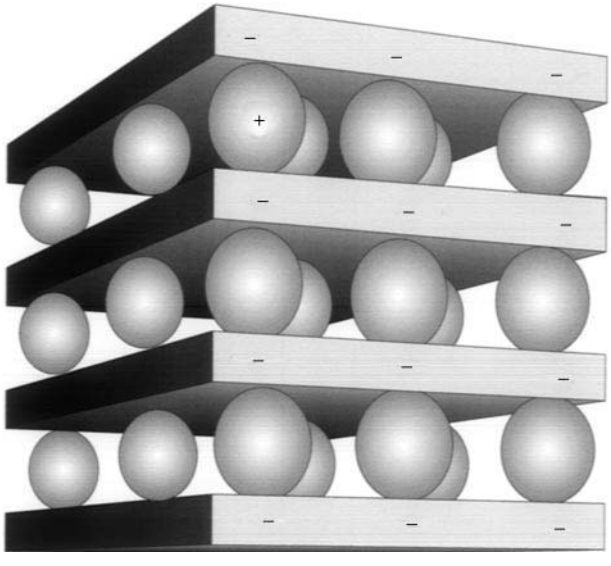

**Figure 12** Schematic representation of a pillared layered structure showing the microporosity and the diffusion paths.

when the first Zr(IV) phosphonates and Zr(IV) organophosphates with formula $Zr(RPO_3)_2$ or $Zr(ROPO_3)_2$ respectively, were prepared (R being an organic group). These compounds are organic derivatives of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ in which the –OH groups attached to the phosphorous atoms have been replaced by organic R groups, leaving the inorganic structure of the $\alpha$-layer essentially unchanged.

A further development in layered metal(IV) phosphates was achieved with the resolution of the structure of the $\gamma$-phases and with the discovery that it is possible to replace interlayer dihydrogenphosphate groups by monovalent phosphonate or phosphinate anions by simple topotactic anion exchange reactions (see above).

Nowadays, a large number of metal(IV) phosphonates of $\alpha$- and $\gamma$-type are known and many others can be prepared for special purposes, constituting a very large and versatile class of layered materials. A brief account of preparation procedures, structural

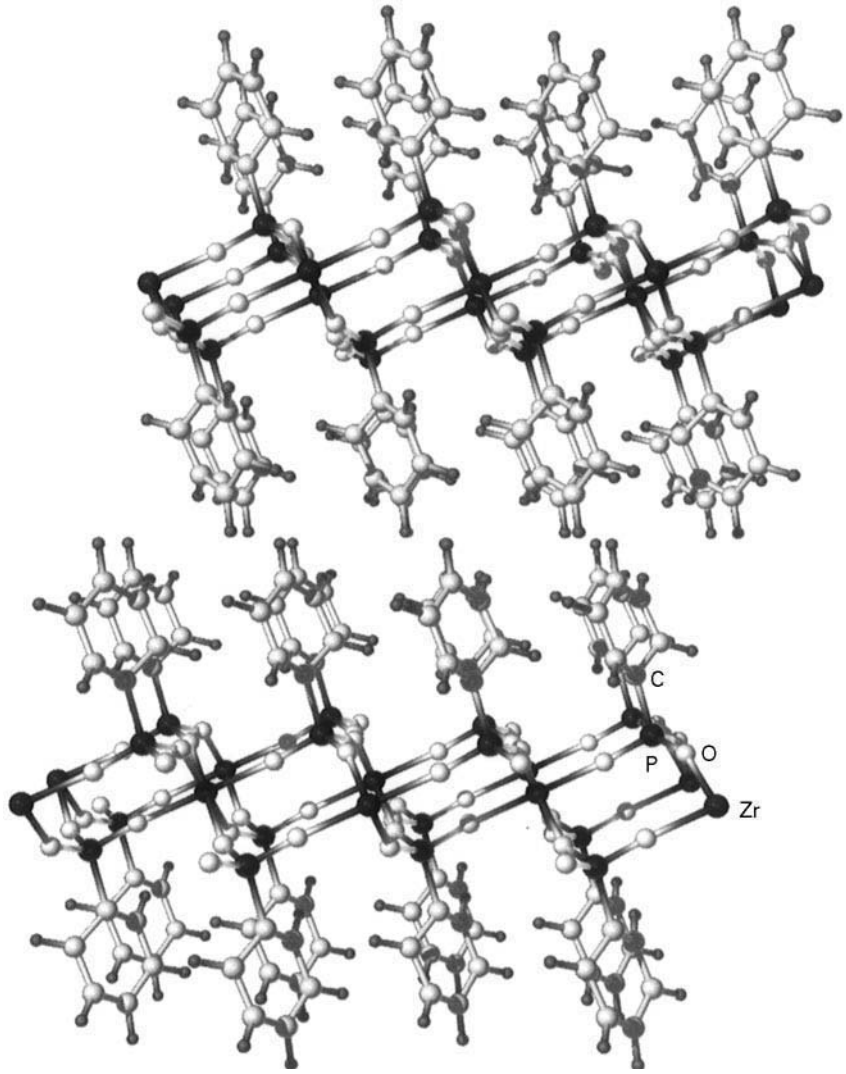


**Figure 13** Computer-generated representation of the sequence of two layers of $\alpha$-$Zr(C_6H_5PO_3)_2$. (Data from Alberti G, Costantino U, Allulli S and Tomassini N (1978) *Journal of Inorganic and Nuclear Chemistry* 40: 1113–1117, with permission from Elsevier Science.)

features and the chemistry of $\alpha$- and $\gamma$-zirconium phosphonates is given.

### Zirconium Phosphonates of $\alpha$-Type

The preparation of Zr phosphonates is closely related to the methods employed for the preparation of $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$, i.e. refluxing of amorphous precipitates with solutions containing the chosen phosphonic acids, and the direct precipitation method in the presence of Zr fluorocomplexes and the suitable $H_2O_3PR$ acid.

As already mentioned, the layer structure arises from the concatenation of $ZrO_6$ octahedra and $O_3PR$ tetrahedra similar to that present in $\alpha$-zirconium phosphate. Due to the short lateral distance between adjacent $O_3P$–R groups on each side of the $\alpha$-layer (5.3 Å) interpenetration of the R-groups belonging to adjacent layers cannot occur for steric reasons and a double film of R-groups is expected for all the members of this class. Therefore these organic derivatives have a layered structure similar to that of zirconium benzenephosphonate (see **Figure 13**) or zirconium carboxyethanphosphonate (see **Figure 14**), two typical compounds of the class.

A list of selected $\alpha$-layered phosphonates is given in **Table 4**. Note that the compounds contain a variety of functional groups. By choosing appropriate organic groups attached to the phosphorus atom, it is possible to vary the acid properties of the phosphonates from neutral (e.g. P–$CH_3$) or weakly acid (e.g. P–$CH_2COOH$) to strongly acid (e.g. P–$C_6H_4SO_3H$) or even to basic (e.g. P–$C_2H_4NH_2$), or to anchor the amino acid chiral group. The nature of the covalently

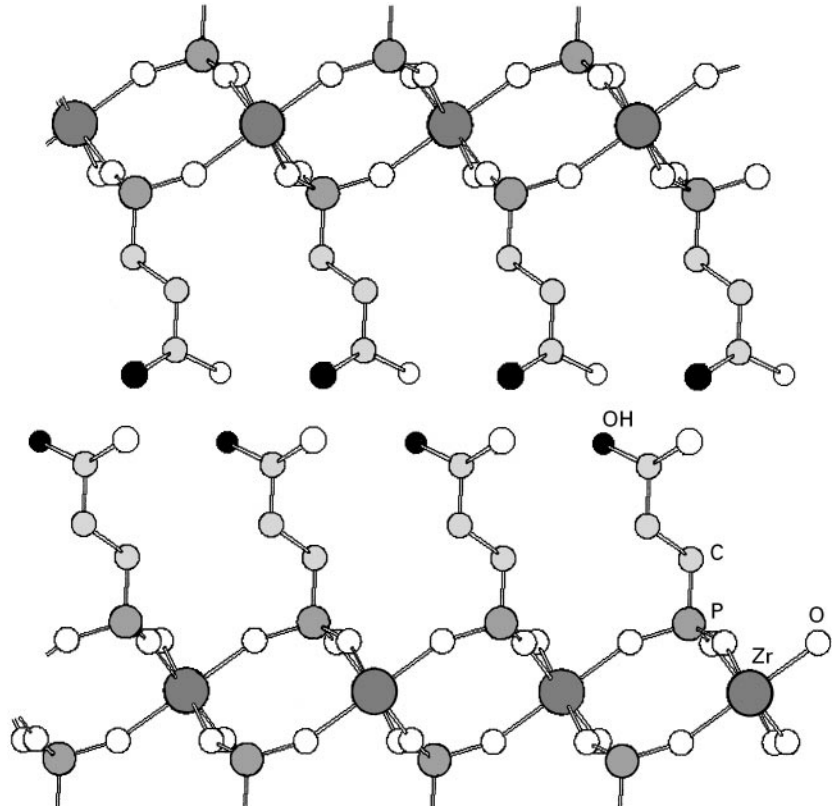


**Figure 14** Computer-generated representation of the sequence of two layers of α-$Zr(HOOCCH_2CH_2PO_3)_2$. (Data from Alberti G, Costantino U, Casciola M, Vivani R and Peraio A (1991) *Solid State Ionics* 46: 61–68, with permission from Elsevier Science.)

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attached groups depends on the imagination and ability of the chemist to synthesize the appropriate phosphonic acids.

The only limitation to synthesis is the use of organic groups with a cross-section equal to or less than 24 $Å^2$. This is the free area around each P–OH group present on the surfaces of the layers of the parent α-$Zr(HPO_4)_2$. However, more voluminous groups may be attached to the α-layers if their dimensions are compensated by introducing small groups R′ (R′ being H, OH, $CH_3$) to obtain compounds of formula $Zr(RPO_3)_{2-x}(R'PO_3)_x$. These mixed component phases are of great interest since a very special type of complexing agent or redox couple may be fixed to the layers. A selection of the multicomponent phases prepared to date is given in **Table 5**.

Zirconium diphosphonates, of general formula $Zr(O_3P–R–PO_3)$, in which adjacent inorganic layers of the α-type are covalently joined to each other by divalent organic groups, may also be obtained. These zirconium phosphates do not possess interlayer microporosity, because the distance between adjacent pillars is 5.3 Å and the van der Waals diameter of the alkyl or aryl pillar is about 4 Å. It is however possible to create microporosity in the interlayer region if some pillars are replaced by small $O_3P–H$ groups, and if the pillar has been suitably designed. By using a pillar with bases, such as 3,3′,5,5′-tetramethylbiphenyldiphosphonic acid, a pillared compound exhibiting a high phosphite percentage and interlayer microporosity of 375 $m^2\,g^{-1}$, has recently been prepared.

**Table 4** Interlayer distances of some zirconium *bis*-monophosphonates and organophosphates with α-layered structure

| *Compound* | *Interlayer distance (Å)* |
|---|---|
| $Zr(O_3PCH_3)_2$ | 8.9 |
| $Zr(O_3PCH_2OH)_2H_2O$ | 10.1 |
| $Zr(O_3PCH_2Cl)_2$ | 10.1 |
| $Zr(O_3PCH_2CN)_2$ | 10.8 |
| $Zr(O_3PC_3H_7)_2$ | 14.0 |
| $Zr(O_3P(CH_2)_2COCl)_2$ | 13.5 |
| $Zr(O_3PCH_2COOH)_2$ | 11.3 |
| $Zr(O_3P(CH_2)_2COOH)_2$ | 13.0 |
| $Zr(O_3P(CH_2)_3COOH)_2$ | 15.0 |
| $Zr(O_3PCH{=}CH_2)$ | 10.6 |
| $Zr(O_3PCH_2SO_3H)_2$ | 15.4 |
| $Zr[(O_3PO)(CH_2CH_2O)_nPO_3]$ | |
| $Zr[(O_3PO)(CH_2CH_2NH_2)_2]\cdot 2HCl$ | 14.3 |
| $Zr[HOOCCH(NH_2)CH_2OPO_3]_2$ | 14.5 |

**Table 5** Compositions and interlayer distances of some derivatives of α-zirconium phosphate with two different pendant groups

| *Compound* | *Interlayer distance (Å)* |
|---|---|
| $Zr(O_3POH)_{0.66}(O_3PH)_{1.34}$ | 6.5 |
| $Zr(O_3POH)_{1.15}(O_3PC_6H_5)_{0.85}$ | 12.4 |
| $Zr(O_3POH)(O_3PC_2H_4COOH)$ | 12.9 |
| $Zr(O_3PCH_2OH)(O_3PH)$ | 7.0 |
| $Zr(O_3PC_2H_4COOH)_{1.25}(O_3PCH_2OH)_{0.75}$ | 13.6 |
| $Zr(O_3PC_6H_5)(O_3PH)$ | 10.5 |
| $Zr(O_3PC_6H_4SO_3H)_{0.85}(O_3PC_2H_5)_{1.15} \cdot 3.7H_2O$ | 18.5 |
| $Zr(O_3PC_6H_4SO_3H)_{0.97}(O_3PCH_2OH)_{1.03} \cdot 4.9H_2O$ | 19.6 |

A computer-generated structural model of this microporous pillared compound is shown in **Figure 15**.

### Zirconium Phosphate Phosphonates of γ-Type

The structure of the γ-layer differs from that of the α-layer since the $ZrO_6$ octahedra are placed in two different planes and joined to each other by $PO_4$ tetrahedra. Due to the fact that only three oxygens are available in phosphonate groups, pure γ-zirconium phosphonates cannot exist. However, it is possible to replace the interlayer $H_2PO_4$ groups by monovalent phosphonate or phosphinate anions to obtain layered inorganic–organic derivatives in which the inorganic layer regularly alternates with organic layers. These materials are obtained from a simple topotactic reaction by contacting the original zirconium phosphate microcrystals with a solution of a suitable phosphonic acid. As we have already seen this reaction is similar to an anion exchange process. The texture of the γ-layer remains practically unchanged and it is therefore possible to predict the arrangement of the organic groups in the interlayer region by considering the interlayer distance and the dimension of the groups. **Figure 16** shows the probable structure of γ-zirconium phosphate benzene-phosphonate.

Many organic derivatives have been prepared with this simple procedure including pillared compounds with regular interlayer porosity obtained by partial replacement of the dihydrogenphosphates with bivalent diphosphonate groups. A selected number of recently prepared compounds is reported in Table 6. Monophosphonic or biphosphonic acids containing crown ethers have also been used for the topotactic reaction and compounds with crown ethers covalently attached to the inorganic layers have been obtained. These materials show promise for interesting applications in ionic or molecular recognition and hence for performing selective separations. The γ-system is thus very versatile and the interlayer region can easily be engineered with a large variety of organic groups to obtain materials for application in several fields including the preparation of new stationary phases for chromatographic separation.

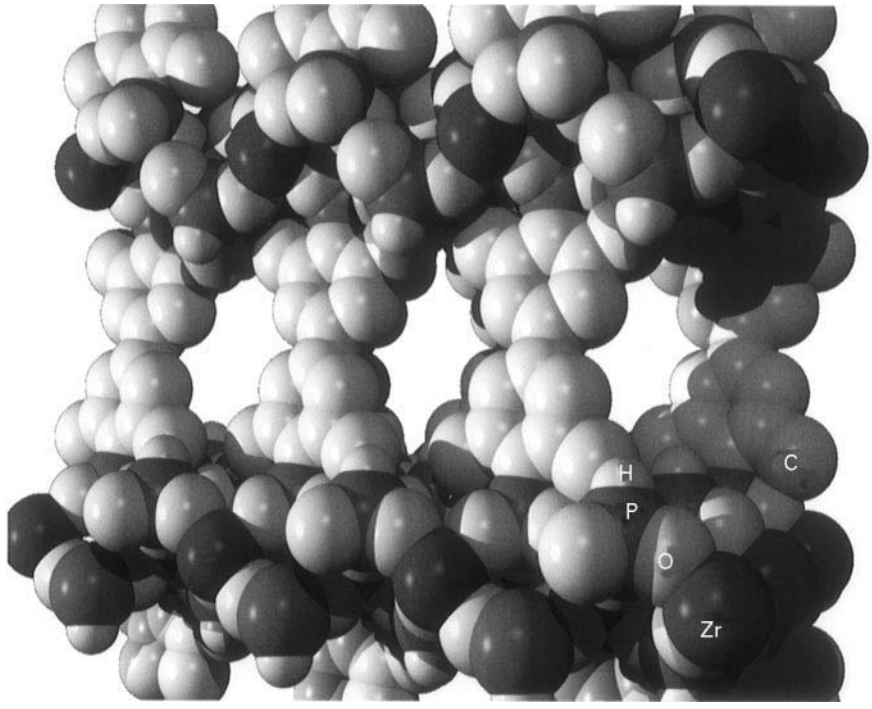


**Figure 15** Computer-generated structural model of a microporous α-zirconium phosphite-diphosphonate. (Data from Alberti G, Costantino U, Marmottini F, Vivani R and Zappelli P (1993) *Angew. Chem. Int. Ed. Engl.* 32: 1357–1359.)

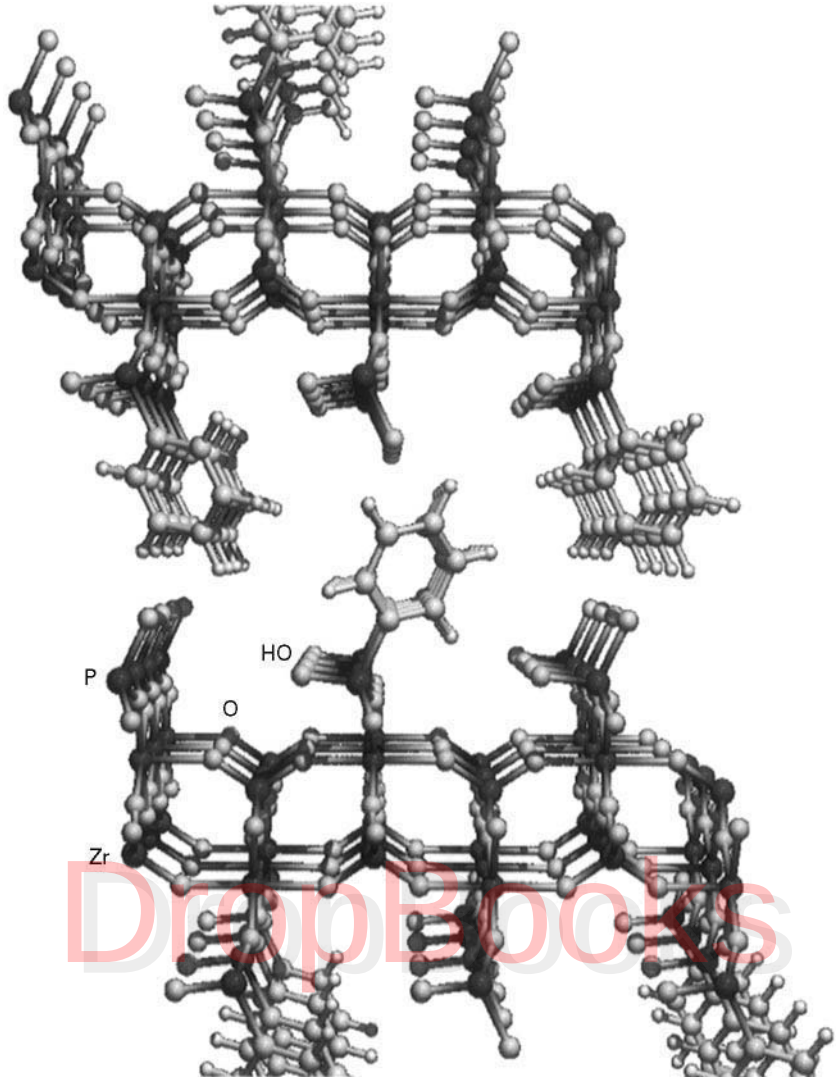


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**Figure 16** Computer-generated representation of the sequence of two layers of γ-zirconium phosphate-benzenephosphonate. (Data from Alberti G, Vivani R, Biswas RK and Murcia-Mascaros S (1993) *React. Polym.* 19: 1–12, with permission from Elsevier Science.)

## Conclusion

The layered phosphates of polyvalent metals are obtained with different layer structures and exhibit a rich chemistry. Many of them are inorganic ion exchangers that support the most common organic resins in processes which occur at high temperatures or in the presence of strong oxidizing solutions and

**Table 6** Composition and interlayer distances of some organic derivatives of γ-zirconium phosphate obtained by topotactic exchange reactions

| *Acid used* | *Composition* | *Interlayer distance (Å)* |
|---|---|---|
| $H_3PO_3$ | $ZrPO_4O_2PHOH \cdot 2H_2O$ | 12.2 |
| $H_3PO_2$ | $ZrPO_4O_2PH_2 \cdot H_2O$ | 8.8 |
| $H_2O_3PCH_3$ | $ZrPO_4O_2POHCH_3 \cdot 2H_2O$ | 12.8 |
| $H_2O_3PC_3H_7$ | $ZrPO_4O_2POHC_3H_7 \cdot 1.2H_2O$ | 15.1 |
| $HO_2P(CH_3)_2$ | $ZrPO_4(H_2PO_4)_{0.33}(O_2P(CH_3)_2)_{0.67} \cdot H_2O$ | 10.3 |
| $H_2O_3PC_6H_5$ | $ZrPO_4(H_2PO_4)_{0.33}(O_2POHC_6H_5)_{0.67} \cdot 2H_2O$ | 15.4 |
| $H_2O_3P(C_6H_{11})$ | $ZrPO_4(H_2PO_4)_{0.33}(O_2POHC_6H_{11})_{0.67} \cdot H_2O$ | 16.9 |
| $H_2O_3PC_6H_5$ | $ZrPO_4O_2PHC_6H_5$ | 15.1 |
| $H_2O_3PC_{10}H_{21}NO_3^*$ | $ZrPO_4(H_2PO_4)_{0.71}(C_{10}H_{21}NO_3PO_3)_{0.29}$ | 16.2 |

*N-(phosphonoethyl)aza crown; (12)crown-4.

strong doses of ionizing radiation. Furthermore, these inorganic ion exchangers possess a high ion exchange capacity and some peculiar selectivities. Layered phosphates are good intercalating agents of ionic or polar species. This allows the construction in the interlayer region of supramolecular assemblies with special functionalities in the fields of chromatographic supports, chemical and electrochemical sensors, ion exchange membranes, ionic and molecular recognition and catalysts. The delamination of layered phosphates has permitted the preparation of thin films and coatings and pillared layered structures with accessible microporosity. There are many more possibilities in layered phosphonate chemistry because functional groups may be inserted on alkyl chains or on aryl rings. The field of layered phosphates and phosphonates is in continuous expansion and these materials will find many applications as soon as their potential is realized.

*See also:* **II/Ion Exchange:** Catalysis: Organic Ion Exchangers; Historical Development; Inorganic Ion Exchangers; Novel Layered Materials: Non-Phosphates; Organic Ion Exchangers; Theory of Ion Exchange.

## Further Reading

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# Novel Layered Materials: Non-Phosphates

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## Introduction

In this paper the structure and composition of layered materials (excluding those which contain phosphates) and their modified variants are described. Layered materials are made up of sheets or planes of atoms held together by interplanar forces which are weaker than intraplanar binding forces. This structural set-up allows the insertion of atomic or molecular guest species between the layers. Such insertion (or intercalation) provides a means for controlled variation of the physical and chemical properties of the host layered material over wide ranges to yield new variants of novel layered materials. The intercalated layered materials are also described.

Layered materials may be broadly classified into three groups according to the composition of their layers and the forces that hold the layers together. The interlayer forces determine the inherent ability of he layers to resist distortions involving displacements transverse to the layer planes.

1. Type I layered materials are made up of layers of atomically thin sheets. The neutral layers are held together by van der Waals forces. Examples are graphite and boron nitride. In graphite the layers tend to be 'floppy' and are easily separated with respect to distortions transverse to the layer